Piecewise polynomial interaction natural orbital study of $1s^2$ helium$^a$

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We report here an analysis of extensive configuration interaction (CI) wave functions for the $1s^2$ ground state of the helium atom using piecewise polynomial basis functions. Large numbers of natural radial orbitals (NROs) with $l$ ranging from 0 to 11 have been treated accurately and analyzed systematically. The contribution of each NRO to the total energy is found to follow the formula $\Delta E \sim -0.42(l + 1/2) \times (n+1/2)^{2l+1} a.u.$, where $n$ is the principal quantum number, and the expansion coefficient of the NRO configuration is found to follow the formula, $c \sim -0.35(l + 1/2)^{l/2} (n - 1/2)^{-l/2}$. (The constants for $l = 0$ are a little different). From an examination of the tails of the NROs, we are able to suggest an $l$-dependent universal asymptotic formula, $\rho^{\delta-1}(l+1)^{-\delta} e^{-\delta l}$, where $\delta$ is a constant, where $\delta = 3.04$, and where $l^2/2$ is the ionization potential. The nodes of the NROs are also found to behave in a systematic way that yields valuable information on the choice of basis functions. So-called "L"-limit energies $E_L$, more accurate than any we could find in the literature, have been determined for $L = 0$ through 11, with a final CI energy calculated here of $-2.90370$ a.u. from a wave function containing 118 NROs. The increments $E_L - E_{L-1}$ are found to follow the formula $-0.0740(L + 1)^{2L+1} - 0.031(2L + 1)^{2l+1}$ a.u., which is useful for extrapolation and extension of the CI energy by two significant digits. The $n$- and $l$-dependent formulas for the energy contributions make it possible to estimate the size of a CI calculation required for a given accuracy. The high accuracy of these CI calculations is made possible by the flexibility and numerical stability of piecewise polynomial basis functions.

I. INTRODUCTION

This study was conceived as a demonstration of the high accuracy of electronic energies calculated with piecewise polynomial wave functions through the example of configuration interaction in the helium atom. Though not anticipated, rather striking regularities of natural-orbital-related quantities for helium have emerged, which make this work perhaps equally interesting as a study of helium itself.

In principle, configuration interaction (CI) can exactly represent an electronic wave function, but practice frequently falls short of principle, as is the case for the ground state of the helium atom: the lowest CI energy we could find in the literature, $-2.90344$ a.u., is eight orders of magnitude less accurate than the nonrelativistic energy, $-2.903724377039 a.u.$, calculated by Frankowski and Pekeris. The shortfall has to do with the choice of basis functions and the slow convergence of the CI expansion vs the $n^2$ logarithm containing wave functions specially applicable to helium.

The greater the accuracy, the more terms must be included in the CI wave function, but how many? The quantitative relationship between accuracy and CI "length" does not seem to have received much attention in the literature, perhaps because of practical problems that accompany large conventional bases: numerical instability, sometimes called "cancellation error" or "computational linear dependence," that originates with the finite word size of electronic computers.

The possibility of large, flexible bases, relatively free of "computational linear dependence," is provided by the recently introduced piecewise polynomial (PP) basis functions. Thus a PP basis of dimension 60 was used to obtain the Hartree-Fock energy of helium to approximately $10^{-14}$ a.u. accuracy, $-2.8963799956121 a.u.$, while a PP basis of dimension 36 (CI dimension $1/2 \times 38 \times 37$) yielded a radial limit energy $-2.8790286 a.u.$, accurate to $1.6 \times 10^{-8}$ a.u. In this paper we apply large PP bases to the full CI problem in helium.

The results of large CI calculations are most conveniently analyzed in terms of natural orbitals (NO's) of symmetry $l$ (the precise definition is given below) varies smoothly with $\nu$ and $L$, and it turns out to be approximate by $-0.42(l + 1/2)/(L + \nu - 3/2) a.u.$ Similar empirical formulas can be found for the expansion coefficients of the NO configurations in the CI wave function and for the "L"-limit energies. Such formulas make it possible to estimate the number of configurations required for the CI energy to have a given accuracy. They also make extrapolations unusually straightforward and accurate.

A detailed study of the NO's in helium, particularly where they have nodes, maxima, and minima, also provides one with the characteristics desirable in any a priori basis.

In this paper we carry out CI calculations on $1s^2$ helium using PP bases, transform to natural radial orbitals (NRO's), and analyze the results. Our goals are to develop further the PP method as a tool for electronic structure calculations, to determine quantitatively the rate of convergence of the CI calculation in terms of NRO's, and to determine general characteristics of
higher NRO’s that are useful in understanding the CI process and in choosing efficient bases.

Background information about the PP method is given in Sec. II, and about the NO method in Sec. III. Technical details of the CI calculation are discussed in Sec. IV and the Appendices. The main results appear in Secs. V–VIII. To aid the reader in keeping track of what information appears where, we list here the principal headings and subheadings:

II. PIECEWISE POLYNOMIAL BASIS FUNCTIONS
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IX. DISCUSSION

ACKNOWLEDGMENT

APPENDIX A. INTEGRALS

APPENDIX B. COMPUTATIONAL DETAILS

APPENDIX C. ADDENDUM ON EQUATIONS (26)–(29)

II. PIECEWISE POLYNOMIAL BASIS FUNCTIONS

The basis functions we use here have the form, \( r' Y_l^m(\theta, \phi) \) times a PP function of \( r \), where \( Y_l^m(\theta, \phi) \) denotes, as usual, a spherical harmonic. That is, we separate out the radial factor \( r' R(r) \) of an atomic orbital,

\[
\psi(r, \theta, \phi) = r' R(r) Y_l^m(\theta, \phi),
\]

and we take \( R(r) \) to be a PP. To fix \( R(r) \), it is first necessary to subdivide the positive \( r \) axis by mesh points,

\[
y_0 = 0 < y_1 < y_2 \cdots < y_N < \infty.
\]

\( R(r) \) is a polynomial on each subinterval \([y_{\nu-1}, y_\nu]\), but the polynomials of different subintervals are not identical. There are several different classes of PP’s that differ in the degree of the polynomial, in the number of derivatives that remain continuous at each mesh point, and in the choice of the mesh itself.

A. Hermite interpolation functions vs splines

Let us require that \( R \) and its first \( s \) derivatives, \( R^{(n)}(n = 0, 1, \ldots, s) \), remain continuous at each mesh point, and consider the implications of fixing the degree of the polynomials. If the degree is \( 2s + 1 \), then the \( 2s + 2 \) polynomial coefficients for the subinterval \([y_{\nu-1}, y_\nu]\) can be chosen to give arbitrary values to \( R \) and its first \( s \) derivatives at \( r = y_{\nu-1} \) and \( r = y_\nu \). Conversely, we may assign \( R^{(n)}(y_{\nu-1}) \) and \( R^{(n)}(y_\nu) (n = 0, 1, \ldots, s) \) arbitrary values, and these values uniquely determine a polynomial of degree \( 2s + 1 \) on \([y_{\nu-1}, y_\nu]\). The required polynomial is given by Hermite’s interpolation formula,\(^9\) and we have referred to this as the Hermite interpolation function (HIF) case.\(^9,10\)

If the degree is less than \( 2s + 1 \), then the \( (s + 1) \times (N + 1) \) values of \( R^{(n)}(y_p) \), \((0 \leq n \leq s)\) and \( 0 \leq p \leq N \), are not all independent but are connected by continuity requirements. Solution of simultaneous linear equations is required before the polynomial coefficients can be determined. These cases constitute the spline methods.\(^9,11\)

If the degree is greater than \( 2s + 1 \), then it is possible to specify arbitrarily the values of left and right derivatives (of higher orders than \( s \)) at each mesh point. Such flexibility to specify higher-order discontinuities is probably unwarranted.

We have found the HIF case to be most convenient and useful in the past,\textsuperscript{9,10} and that is the only PP case we consider in this paper.

### B. MOUND basis functions

Within the vector space of HIF–PP’s for a given mesh, there is a natural set of localized, \textit{continuous} basis functions that have a "unit-\textit{n}th-derivative" property. Each such basis function is nonzero on at most two adjacent subintervals, and each basis function and its first \( s \) derivatives are zero at every mesh point, except for one derivative, say the \( n \)th, whose value is unity at only mesh point, say \( r_n \):

\[
(\frac{d}{dr})^n \chi_{pm}(r) \bigg|_{r=r_n} = \delta_{mn} \delta_{pm} , \quad (k \leq s) .
\]

These "mesh-oriented unit-\textit{n}th-derivative" (MOUND) functions are illustrated in Fig. 1, and they are defined via Hermite’s interpolation formula by\textsuperscript{10}

\[
\chi_{pm}(r) \equiv 0 , \quad (r \leq r_{p-1}, \quad r \geq r_{p+1}),
\]

\[
= \sum_{\text{sub}} \frac{(2k-n)}{k} \frac{(-1)^n}{(2k-n)n!} (r_g - r_{p-1})^{k-n} \cdot (r_g - r)^n (r - r_{p-1})^{k-n} \cdot (r - r_g)^{k-n} ,
\]

\[
(\chi_{p-1} \leq r \leq \chi_{p+1}) ,
\]

\[
= \sum_{\text{sub}} \frac{(2k-n)}{k} \frac{1}{(2k-n)n!} (r_g - r_{p-1})^{k-n} \cdot (r_g - r)^n (r - r_{p-1})^{k-n} \cdot (r - r_g)^{k-n} ,
\]

\[
(\chi_{p-1} \leq r \leq \chi_{p+1}) .
\]

If \( R(r) \) is any PP–HIF function of degree \( 2s + 1 \), then the expansion coefficients of \( R(r) \) on the MOUND basis are just the values of \( R \) and its first \( s \) derivatives at the mesh points.

\[
R(r) = \sum_{\alpha=0}^{s} \sum_{\beta=0}^{s} R^{(\alpha)}(r_{\beta}) \chi_{\alpha}(r) .
\]

### C. Boundary condition at \( r_N \)

Beyond \( r_N \) we take the radial functions to be identically zero,

\[
R(r) = 0 , \quad r \geq r_N .
\]

Clearly \( r_N \) must be sufficiently large for the confinement within \( r_N \) to be inconsequential for the treatment of an atom. As a consequence of this boundary condition (and continuity of \( s \) derivatives at \( r_N \)), the upper limit for \( p \) in Eq. (7) is effectively \( N - 1 \). Thus the \( \{ \chi_{pm} | 0 \leq n \leq s, \quad 0 \leq p \leq N - 1 \} \) form an \((s+1) \times N\) dimensional, nonorthogonal MOUND basis for the representation of \( R(r) \).

### D. Evaluation of one- and two-electron integrals

The evaluation of overlap, kinetic energy, \( 1/r_1 \), and \( 1/r_{12} \) integrals has been given previously for \( s \) orbitals.\textsuperscript{9} Integrals for arbitrary \( l \) and \( m \) are similar to the \( s \) case and are given in Appendix A. The reason for separating out \( r_1 \) in the definition of \( R \) in Eq. (1) is to simplify the \( 1/r_{12} \) integrals. After calculation of the Hamiltonian and overlap matrices with respect to the MOUND functions, the rest of the CI calculation proceeds, as with any basis, completely independently of the nature of the basis.

For the ground state of helium, higher \( l \) orbitals are always coupled together to give \( ^3S \). The consequences of this coupling are incorporated into the formulas of Appendix A.

Although all the integrals are elementary, we note that the number of terms in the final formulas are much larger for PP’s than for Slaters, in that the former depend on up to \((s+1)\times N\) parameters, whereas the latter depend only on two \("w" \) and \("z")

### E. Dependence of representation error on mesh and degree

The error in the representation of an arbitrary function by a HIF polynomial on the interval \([r_{p-1}, r_p]\) is given by a mean value theorem\textsuperscript{14}:

\[
\delta R(r) = (r - r_{p-1})^{s+1}(r - r)^{s+1} R((s+2))/(2s+2)! .
\]

The error for the Hartree–Fock case in helium is particularly easy to analyze with this formula, because there is only one \( R(r) \) involved, and that \( R(r) \) is approximately exponential. "Logarithmic" meshes are especially suitable, and the error in the calculated Hartree–Fock energy depends\textsuperscript{9} on the polynomial degree \( 2s + 1 \) and on the number \( N \) of subintervals according to

\[
\delta E_{\text{HF}} \sim N^{-((s+2))} .
\]

The error in the CI case is not so easy to analyze quantitatively with the same formula (9), because there are many \( R(r) \) involved, and their behavior is more complicated than a simple exponential. One can make a crude argument that gives a formula similar to (10). The error in any particular \( R(r) \) is of order \( 2s + 2 \) in
while the error in $dR/dr$ is of order $2s+1$.

The contribution of the errors of any fixed set of $R(r)$ to the total kinetic energy error (cf. Ref. 9) is quadratic in the $\delta(R/dr)$, then times a typical subinterval length $[r_{p_{1/2}}, dr]$ and times the number of subintervals ($N$). Thus, for a family of meshes for which the typical subinterval length scales like $1/N$ from one mesh to the next, and for a CI wave function in which the number and type of configurations is held constant, one is led to a formula similar to (10),

$$\delta E_{CI}(\text{mesh and degree error}) \sim N^{-1(4s+2)} . \tag{11}$$

This error formula (11) is for a "fixed form" CI wave function as $N$ and $s$ are increased. There is, however, the equally (if not more) important question of how many NRO's can be accurately represented with PP's of a given mesh and degree—i.e., with fixed $N$ and $s$, but with increasing CI. To this question we can only give an empirical answer, discussed in Sec. III F.

III. NATURAL ORBITAL EXPANSION FOR $1s^2$ HELIUM

A. Definition

The most rapidly converging CI expansion for a two-electron wave function is provided by L"avadin's natural orbitals,$^{11}$ when convergence is measured by the overlap of the approximate CI wave function with the exact wave function.$^{12}$ Expressed in terms of NRO's, the ground state CI wave function for helium has the canonical form,

$$\psi(1, 2) = \sum \phi_{\nu}(1) R_{\nu}(r_1) \phi_{\nu}(2) R_{\nu}(r_2) \times (2l + 1)^{1/2} \sum \phi_{\nu}^{*}(\theta_1, \phi_1) \phi_{\nu}^{*}(\theta_2, \phi_2) (\alpha \beta - \beta \alpha) / \sqrt{2} . \tag{12}$$

As emphasized by Davidson,$^{21,22}$ the canonical form (12) is the best way to define the NO's in the two-electron case.

B. Usefulness

At the start of a CI calculation, one normally does not have the NRO's; they are found at the end of the CI calculation by transformation to the canonical form (12). (We have not pursued here the self-consistent NRO approach developed especially by Kutzelnigg,$^{23,24}$ among others.$^{11,24-28}$) The usefulness of NRO's here is fivefold:

(1) NRO's permit one to gauge the convergence of the CI expansion. By using truncated CI wave functions, one can compute various quantities as a function of the number of NRO's included, extrapolate to an infinite expansion, and so obtain a measure of the convergence of the CI energy and wave function. The most extensive NRO analysis of $1s^2$ helium to date has been that of Bunge.$^{27}$

(2) Besides permitting an estimate of what is explicitly left out of the CI expansion, NRO's also permit an estimate of the accuracy of what is put in. NRO's are independent of the basis, if the basis is complete. In practice, bases are never complete, the wave function is only an approximation to the exact one, and consequently the NRO's calculated are only approximate. Comparison of various NRO-related quantities calculated in successively "more complete" bases yields a measure of the accuracy of the final NRO's in the "best" basis.

(3) Since NRO's are independent of the basis (for complete bases), NRO's permit detailed comparisons with other calculations that may use completely different bases.

(4) NRO's are the ultimate model for choosing basis functions. The choice of basis has long been recognized as crucial to accuracy. Boys,$^4$ and Taylor and Parr$^3$ formulated a rule-of-thumb a principle of "maximum radial overlap" for STO's. Since NRO's provide the most efficient CI representation, the ultimate principle behind all such rules—of-thumb is for the basis to be able to represent a maximum number of NRO's. In the case of PP bases, by examining NRO's in successively better bases, we are able to infer a rule for choosing the mesh points.

(5) The "best convergence" property of NRO's permits one to reduce the size of the CI calculations, as discussed in Secs. III E and IV.

C. Energy increment associated with NRO $r' R_{\nu}$

We wish to define an energy increment $\Delta E_{\nu}$ associated with NRO $r' R_{\nu}$, that will play a key role in our analyses. Of many possible definitions, we choose an operationally simple one, similar to that of Bunge,$^{27}$ based on truncating (with no reoptimizing) a CI wave function. We take $\Delta E_{\nu}$ to be the difference of two expectation values: the first with respect to the CI wave function truncated by dropping all $R_{\nu}$, with any $\nu'$ and with $l' > l$, and all $R_{\nu'}$ with $\nu > \nu'$; the second with respect to the first truncated wave function, but with the configuration of $R_{\nu}$ dropped. More precisely, denote the doubly occupied NRO configurations by

$$\phi_{\nu}(1, 2) = r_{\nu}^{1/2} R_{\nu}(r_1) r_{\nu}^{1/2} R_{\nu}(r_2) (2l + 1)^{1/2} \times \sum \phi_{\nu}^{*}(\theta_1, \phi_1) \phi_{\nu}^{*}(\theta_2, \phi_2) (\alpha \beta - \beta \alpha) / \sqrt{2} . \tag{13}$$

so that the CI wave function (12) can be written

$$\psi(1, 2) = \sum \phi_{\nu}(1, 2) . \tag{14}$$

Define $\psi_{\nu}(1, 2)$ and $\overline{\psi}_{\nu}(1, 2)$ by

$$\psi_{\nu}(1, 2) = \sum_{l' \not= \nu} c_{\nu l'} \phi_{\nu l'}(1, 2) + \sum_{\nu > \nu} c_{\nu l} \phi_{\nu l}(1, 2) , \tag{15}$$

$$\overline{\psi}_{\nu}(1, 2) = \psi_{\nu}(1, 2) - c_{\nu l} \phi_{\nu l}(1, 2) . \tag{16}$$

Then, by $\Delta E_{\nu}$, we mean

$$\Delta E_{\nu} = \langle \phi_{\nu} | H | \phi_{\nu} \rangle - \langle \overline{\psi}_{\nu} | H | \overline{\psi}_{\nu} \rangle . \tag{17}$$

For the special case $(\nu, l) = (1, 0)$, there is no $\overline{\psi}_{10}$, and $\Delta E_{10}$ is just the expectation value of $H$ with respect to the doubly occupied $1s$ NRO.

One must distinguish the $\Delta E_{\nu}$ obtained in a practical calculation from the ultimate $\Delta E_{\nu}$ extracted from the exact wave function. The $\Delta E_{\nu}$ will vary as the basis is
changed and as the number of configurations in the CI wave function (before truncation to get $\psi_L$) is changed. It is by monitoring the changes in the $\Delta E_{v1}$ as the total number of configurations in the CI wave function is changed that one can estimate the accuracy of the final $\Delta E_{v1}$.

D. "L"-limits, $E_L$, and $\Delta E_L$

The "L"-limit energy $E_L$ is the lowest energy obtained from a CI wave function containing no basis function with $L > L$. We define $\Delta E_L$ to be the difference of the two CI energies,

$$\Delta E_L = E_L - E_L^{-1}, \quad (L \geq 1),$$

$$\Delta E_0 = E_0.$$  \hfill (18)

$\Delta E_L$ is only approximately equal to $\sum_v \Delta E_{vL}$.

$$\Delta E_L = \sum_v \Delta E_{vL}.$$ \hfill (19)

The lack of equality results from the three different CI wave functions involved: the "L" limit, the "L = 1" limit, and the exact CI wave functions. We use "L" limit generically for S limit, $P$ limit, etc. The quotes are to avoid confusion with the $L = 8$ case, for which the spectroscopic symbol is also $L$. We do not refer to $E_S$, $E_P$, etc., but rather to $E_0$, $E_1$, etc.

E. Stepwise procedure for generating CI wavefunctions: general features

All the calculations described in the next section follow a sequential pattern characterized by proceeding from one "L" limit to the next. At the $S$ limit step, a complete CI is followed by a transformation to NRO’s and a selection of only some of the $S$-NRO’s to be used as basis functions for higher "L" limits. At the $P$-limit step, all possible $ss'$ configurations made from the selected $s$-NRO’s and all possible $pp'$ configurations are used to get a CI wavefunction, that is then transformed to canonical form. Only some of the $P$-NRO’s are selected to be included with the previously selected $s$-NRO’s from the $S$ limit to be used in the calculation of the $D$-limit wave function. Note that the $s$-NRO’s obtained from the $P$ limit are different from the $s$-NRO’s obtained from the $S$ limit, but no reduction in their number is made between the $P$- and $D$-limit calculations. Consequently, their CI spaces are the same, and there is no reason or benefit to change the input to the $D$-limit calculation from $S$-limit to $P$-limit $s$-NRO’s.

In such a sequential manner, with two exceptions noted later, three sets of calculations were carried out leading to $D$-limit, $G$-limit, and $O$-limit wave functions.

F. Observations on the influence of mesh and degree on the accuracy of NRO’s

In the exponential-like Hartree–Fock case, it was possible to "derive" from Eq. (10) a logarithmic formula for a "suitable" mesh. In the CI case, with many $R_{ij}$ to represent, such a simple analysis seems to be precluded.

We have instead taken the "brute force" approach of carrying out several exploratory CI calculations with different meshes and degrees, and then analyzing the resultant $\Delta E_{v1}$ and $R_{ij}$ for regularities and the onset of irregularities. We found the following:

(1) For fixed $l$, $\Delta E_{v1}$ is approximately proportional to the inverse sixth power of the principal quantum number, $\nu + \nu$. (Cf. Bange.\textsuperscript{27})

(2) Within a given basis, $\Delta E_{v1}$, $\Delta E_{v2}$, ..., would be accurate up to, say, $\Delta E_{v1}$, after which the $\Delta E_{v1}$ would be grossly inaccurate.

(3) Examination of the NRO’s $R_{ij}$, $R_{kl}$, ..., revealed that when $\Delta E_{v1}$ is accurate, $R_{ij}$ has no more than $s$ nodes in any subinterval, but that when $\Delta E_{v1}$ is inaccurate, $R_{ij}$ has generally $s + 1$ or more nodes in at least one subinterval.

(4) The "measure of accuracy" is given roughly by the order of magnitude of the last accurate $\Delta E_{v1}$ ($l$ fixed).

From these observations, we can infer that the mesh should be chosen so that the number of nodes of as many NRO’s as possible is not greater than $s$ in any subinterval.

With a given mesh and degree, the dimension of the MOUND basis is $(s + 1)N$. Note that $R_{ij}$ has $\nu - 1$ nodes; when $\nu = sN + 2$, there is at least one subinterval with $s + 1$ or more nodes, no matter how the mesh is chosen. Thus, there cannot be more than $sN - 1$ NRO’s for each $l$ with $s$ or fewer nodes per interval, and the maximum "efficiency" of the PP basis is empirically

$$(sN + 1)/[(s + 1)N] - s/(s + 1).$$ \hfill (21)

Basis efficiency and high accuracy favor high $s$, but computer time and storage requirements favor small $s$. Our most accurate calculations for small $l$ values were carried out with $s = 3$ and $N = 9$, while our most extensive high $l$ calculations necessitated dropping $s$ to 2.

IV. CHOICE OF MESH AND DEGREE; SELECTION OF NATURAL ORBITALS IN ACTUAL COMPUTATIONS

To take into account the relationship between accuracy and the NRO nodes and mesh, as discussed in Sec. III F, it is necessary to know the locations of the nodes of a good number of NRO’s. The nodes can be located for the first several NRO’s by preliminary calculations, and the nodes of the higher NRO’s can be estimated from the lower ones. A more complete discussion of the NRO nodes is given in Sec. VA.

We describe here three sets of CI calculations: a $D$-limit series, a $G$-limit series, and an $O$-limit series. In all three, the number of subintervals is $N = 9$. In the first two the polynomial degree $2s + 1 = 7$, while in the $O$-limit series the degree is $2s + 1 = 5$. We shall indicate these values of $s$ and $N$ by the prefixes "$3-9$", "$3-9$", and "$2-9$", respectively.

A. $D$-limit series

In the first series of calculations we aimed for approximately $10^{-6}$ a.u., accuracy for the $S_2$, $P_4$, and $D$-limit energies. We took $s = 3$ and selected a Hartree–Fock mesh ("$P$" in Table IV of Ref. 9) that gave $10^{-6}$
TABLE I. Mesh points, in atomic units.

<table>
<thead>
<tr>
<th></th>
<th>r_0</th>
<th>r_1</th>
<th>r_2</th>
<th>r_3</th>
<th>r_4</th>
<th>r_5</th>
<th>r_6</th>
<th>r_7</th>
<th>r_8</th>
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</tr>
</thead>
<tbody>
<tr>
<td>3-9&quot; calculations</td>
<td>0.31</td>
<td>0.58</td>
<td>0.92</td>
<td>1.33</td>
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<tr>
<td>2-9&quot; calculations</td>
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<td>1.65</td>
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<td>6.40</td>
<td>10.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a.u., accuracy at the Hartree–Fock (HF) level. This mesh had N' = 6, but it turned out to be adequate for only nine s-NRO's. The tenth already had five nodes in the first subinterval. Consequently we added three points in the region, r < 3.5, and readjusted the other points to straddle better the nodes of higher R_{nl}. The revised mesh, listed in Table I, gives a MOUND basis of dimension 36 per l value, and it yielded a HF energy of -2.86167 99953 78 a.u., of 2.34 \times 10^{-10} a.u. accuracy. The adjusted mesh was adequate for 24 s-, 24 p- and 24 d-NRO's.

It was by examining the ΔE_{nl} as described in Sec. III E, that it became clear that the last 12 s-NRO’s, and also p-NRO’s, were inaccurate and were largely artifact, and so only the first 24 S-limit s-NRO’s were used in the F-limit calculation, and only the first 24 F-limit p-NRO’s were used (with the 24 S-limit s-NRO’s) in the D-limit calculation. The “theoretical” maximum of 27 “good” NRO’s was not quite realized, because some mesh points were needed for the tail region, whereas the nodes occurred at shorter distances.

B. G-limit series

Because of limits on the availability of computer time and storage, we decided to reduce further the number of s-, p-, and d-NRO’s before continuing on to the F and G limits. Accordingly we took the first 15 NRO’s of s, p, and d symmetry from the D-limit calculation, and we revised our accuracy goal to 5 \times 10^{-7} a.u. Note that the 15 s- and p-NRO’s used as basis functions in the F- and G-limit calculations came from the D-limit CI and not directly from the S- and P-limits. This is the first exception to the general scheme outlined in Sec. III E.

In proceeding from the F- to G-limit CI, we more conservatively kept 18 f-NRO’s.

C. O-limit series

From the D-limit and G-limit calculations, we were able to gauge more accurately: (i) the locations of the nodes of higher R_{nl}, which displayed an unexpected bunching phenomenon described in Sec. V A; (ii) the behavior of the ΔE_{nl} and ΔC_{nl} for increasing L, ν, and l; and (iii) the requirements for CPU time, core, and disk storage. Accordingly, we decided to aim for a total energy of -2.90370 a.u., which would occur at about L = 10 or 11, and for this final accuracy (2 \times 10^{-7} a.u.) it was possible both to reduce s to 2 and to select a much smaller number of NRO’s at each step. Also a readjustment was made in the mesh, which is listed in Table I. Note that in the “2-9” calculations, there are 27 MOUND basis functions per l value.

The stepwise CI calculation was carried out as described in Sec. III E, up through l = 8, until a basis of 89 radial orbitals (s^8 p^{10} d^{15} f^{15} g^{10} h^{10} i^{10} l^{10}) has been generated. By this point it was clear that R_{nl} was quite similar to R_{ri}. To save additional time, instead of adding the full 27 l = 9 MOUND functions for the M limit, we instead constructed the l = 9 part of the basis from ten Schmidt-orthogonalized R_{nl}. (For l = 9, the full radial orbital formed from R_{nl} is r^9 R_{nl}; the r^8 R_{nl} are orthogonal, but not r^9 R_{nl}; hence the need for orthogonalization.) Some loss of accuracy in representing the l = 9 NRO’s of course resulted. Similarly for l = 10, we used the 10 R_{nl} NRO functions to make 10 nonorthogonal l = 10 basis functions. Finally, for l = 11, we took only 9 basis functions, because with ten we encountered some numerical difficulties, presumably due to the accumulation of inadequacy in the way the m, n- and o-basis functions were chosen. The modified treatment of l = 9, 10, and 11 is the second exception mentioned in Sec. III E.

V. BEHAVIOR OF NATURAL RADIAL ORBITALS

A. Nodes

To get an overall picture of the NRO’s, the nodes are perhaps the simplest property on which one can focus. The NRO nodes are also a key characterization of what any relevant a priori basis must be able to represent.

We present graphically in Fig. 2 the location of the nodes of those NRO’s from the final O-limit wave function with 2 ≤ ν ≤ 9 and 0 ≤ l ≤ 11. (The NRO’s with ν = 10 are less accurate than the others; see Sec. VI A). The location of any particular node in R_{nl} depends on whether R_{nl} is taken from the “F” limit, the “l = 1” limit, etc., but the variation (≤ 0.01 a.u.) is not significant on the scale of Fig. 2.

What is particularly striking in Fig. 2 is how the nodes of R_{nl}, R_{n1}, ..., R_{n11}, ... are related to each other. As l increases, all the nodes of R_{nl} move in the direction of approximately r = 1.2 a.u. As l increases, but ν remains fixed, the nodes of R_{nl} bunch together.

B. Similarity of r^l R_{nl} for fixed ν

Despite the bunching phenomenon of the nodes, the NRO’s for fixed ν are otherwise qualitatively rather insensitive to l. In Fig. 3, we have plotted r^l R_{nl} for l = 0 through 11, to show how similar the r^l R_{nl} are for fixed ν. This similarity was used to shorten the computational procedure in the M-, N-, and O-limit calculations (Sec. IV C).

C. Spatial localization

The NRO’s are rather localized and show a characteristic behavior as ν increases. In Fig. 4, we have plotted the d-NRO’s, r^l R_{nl}, for ν = 1, 2, ..., 9, to show how dramatically the NRO’s for fixed l stay in the “atomic” region characterized by the 1s NRO, how they reach a higher and
higher maximum closer and closer to the origin, and
how the relative magnitudes of the extrema decrease
monotonically as \( r \) increases. Indeed, Fig. 4 suggests
an envelope for the NRO's of the qualitative shape, \( \pm r^{-4} \).

D. Cusp behavior

As discussed by Pack and Byers-Brown, the NRO's
should satisfy the cusp condition,

\[
R_{nl}(0)/R_{nl}(0) = -2/(l + 1),
\]

where the 2 is the helium nuclear charge. Although it
would have been easy to build the cusp condition into the
basis as a constraint, we did not do so. The ratios
\( R_{nl}(0)/R_{nl}(0) \) for various representative NRO's are
listed in Table II. That the G-limit series gives better
agreement than the O-limit series is simply a consequence of
the higher accuracy of the septic vs quintic polynomials.
That the lower \( l \) NRO's have "better" cusps than
the higher \( l \) NRO's is a consequence of the \( r^{-2l-2} \) "weight-
ing factor" that severely attenuates the energy contribu-
tion of the origin region for higher \( l \), and consequently
the accuracy to which the wave function is obtained.
That the agreement becomes poorer as \( l \) increases is a
similar indication of the smallness of the contribution of
the origin region to the energy, and the consequent im-
precision in that part of the wave function.

E. Tail behavior

The tails of natural orbitals have been the subject of
some controversy. Morrell, Parr, and Levy suggested the asymptotic form,
\[ r^1 R_{1s}(r) = g_{1s}(r) \exp\left[-(-2 \mu_{\text{max}}^{1/2}) r\right], \]  
(23)

but Ahriche\textsuperscript{31} pointed out a nonrigorous interchange of two limit processes in their derivation. He instead proved rigorously the asymptotic inequality,

\[ r^1 |R_{l}(r)| \leq M_{l} r^{-l/2} \exp\left[-(2 \mu_{\text{min}}^{1/2}) r\right]. \]  
(24)

Here \( \mu_{\text{min}} \) is the smallest ionization potential, which is essentially \( \mu_{\text{max}} \), and \( \gamma = 2/(2 \mu_{\text{max}}^{1/2}) \).

We suggest yet a third relation that is compatible with either of the others, but which is consistent with the observation that the helium normal orbitals,

\[ \chi_{l=1}(r, \theta, \phi) = r^1 R_{l=1}(r) Y_l^0(\theta, \phi), \]  
(25)

are eigenfunctions of the operator (see also Appendix C),

\[ \left(-\frac{1}{r^2}\nabla^2 - \frac{2}{r}\right)P + P \left(-\frac{1}{r^2}\nabla^2 - \frac{2}{r}\right)K, \]  
(26)

where \( P \) and \( K \) are weighted total projection and exchange operators,

\[ P = \sum \frac{c_{lm}(2l+1)^{1/2}}{r} \chi_{l=1m}, \]  
(27)

\[ K = \sum \frac{c_{lm}(2l+1)^{1/2}}{r} K_{l=1m}, \]  
(28)

and where \( K_{l=1m} \) is the usual exchange operator associated with orbital \( \chi_{l=1m} \). The suggestion is that each \( r^1 R_{l} \) is asymptotically proportional to \( r^{-l+1} R_{10} \) for \( l > 0 \), and to \( R_{10} \) for \( l = 0 \). That is,

\[ r^1 R_{l}(r) \sim k_{l} r^{-l+1} R_{10}(r), \quad (l \geq 1), \]  
(29a)

\[ 1s \quad -2.000 \quad -2.001 \quad -2.001 \quad -2.001 \quad -2.001 \quad -2.000 \\
2s \quad -2.000 \quad -1.999 \quad -1.998 \quad -1.998 \quad -1.998 \quad -1.993 \\
3s \quad -2.000 \quad -2.000 \quad -2.000 \quad -2.000 \quad -2.000 \quad -1.996 \\
4s \quad -1.999 \quad -1.997 \quad -1.997 \quad -1.997 \quad -1.997 \quad -1.774 \\
5s \quad -2.002 \quad -1.992 \quad -1.992 \quad -1.992 \quad -1.992 \quad -1.774 \\
6s \quad -2.007 \quad -1.991 \quad -1.991 \quad -1.991 \quad -1.991 \quad -0.994 \\
7s \quad -2.024 \quad -1.981 \quad -1.981 \quad -1.981 \quad -1.981 \quad -0.749 \\
8s \quad -2.051 \quad -1.965 \quad -1.964 \quad -1.964 \quad -1.964 \quad -0.149 \\
9s \quad -2.084 \quad -1.881 \quad -1.750 \quad -1.750 \quad -1.884 \quad -0.011 \\
10s \quad -1.842 \quad -1.382 \quad -1.134 \quad -1.022 \quad -0.984 \quad -1.079 \\

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\textbf{orbital} & \textbf{s-limit} & \textbf{p-limit} & \textbf{d-limit} & \textbf{f-limit} & \textbf{g-limit} & \textbf{h-limit} & \textbf{i-limit} \\
\hline
1s & 1.298 & 3.510 & 4.492 & 4.967 & 5.273 & & \\
2s & & & & & & & \\
3s & & & & & & & \\
4s & & & & & & & \\
5s & & & & & & & \\
6s & & & & & & & \\
7s & & & & & & & \\
8s & & & & & & & \\
9s & & & & & & & \\
10s & & & & & & & \\
\hline
\end{tabular}
\caption{Coeff values computed for various natural radial orbitals from the \( ^{2}\text{S} \) and \( ^{2}\text{P} \) levels.}
\end{table}

the entire local contribution to the energy is smaller than the precision of the calculation. Another consideration is that as $r$ approaches $r_h$, the (artificial) boundary condition at $r_h$ makes all orbitals behave like $(r_h - r)^{1/2}$. For these two reasons, if $r$ is too large, the NRO will not be accurate.

Table III. Energy increments $\Delta E$ associated with natural radial orbitals, displayed to illustrate changes from S-limit to D-limit wavefunctions, calculated with *-9" basis, in atomic units.

<table>
<thead>
<tr>
<th>orbital</th>
<th>S-limit</th>
<th>P-limit</th>
<th>D-limit</th>
<th>G-limit</th>
</tr>
</thead>
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<td>-0.001659901</td>
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<td>-0.001659901</td>
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<td>-0.001659901</td>
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<td>-0.001659901</td>
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<td>-0.001659901</td>
<td>-0.001659901</td>
</tr>
<tr>
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<td>-0.001659901</td>
<td>-0.001659901</td>
<td>-0.001659901</td>
</tr>
<tr>
<td>7s</td>
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<td>-0.001659901</td>
<td>-0.001659901</td>
</tr>
<tr>
<td>8s</td>
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<td>-0.001659901</td>
<td>-0.001659901</td>
<td>-0.001659901</td>
</tr>
<tr>
<td>9s</td>
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<td>-0.001659901</td>
<td>-0.001659901</td>
</tr>
<tr>
<td>10s</td>
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<td>-0.001659901</td>
</tr>
<tr>
<td>15s</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Total</td>
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<td>-0.001659901</td>
<td>-0.001659901</td>
<td>-0.001659901</td>
</tr>
</tbody>
</table>

FIG. 5. Tail behavior of natural radial orbitals: logarithmic derivatives of $r^2 R_{2s}$ vs $1/r$. The $r^2 R_{2s}$ are from the "3-9" G-limit wave function. The dashed lines are the logarithmic derivatives of $r^{\gamma} \exp(-\alpha r)$ and $r^{\gamma} \exp(-\alpha r)$ ($\gamma = 1, 2, 3$), where the $1.344 = [2 \times (ionization potential)]^{1/2}$, and the $-0.26 = 1/1.344 - 1$ (see text). The oscillations are presumably artificial and indicate lack of precision in determining the NRO's at large $r$.

\[ R_{2s}(r) = k_{2s} R_{1s}(r), \]  

(29b)

where the $k_{ij}$ are independent of $r$.

One observable consequence of Eq. (29) is that $R_{ij} / R_{1s}$ should be asymptotically constant. If $R_{1s} \approx r^6 \exp(-\gamma r)$, then a second observable consequence should be that the logarithmic derivative of $r^2 R_{1s}$ should go asymptotically like $-\gamma + (\beta - 1 + \delta)/r$.

Before turning to the computations to see what is found, we must first consider how accurately the tails can be computed. The nonrelativistic electronic ionization potential for helium is 0.9037 a.u. The factor $\exp(-2 \times 0.9037)^{1/2}$ falls to $10^{-2}$, $10^{-3}$, and $10^{-4}$ at $r = 3.4, 5.1, \text{ and } 6.9 \text{ a.u.}$, respectively. Since the contribution to the energy is quadratic, $r$ need not be very large before

FIG. 6. Tail behavior of natural radial orbitals: ratio of nth to first orbital of the same I value, for various natural radial orbitals taken from the "3-9" G-limit wave function. The oscillations are presumably artificial and indicate lack of precision in determining the NRO's at large $r$.
On the other hand, if \( r \) is too small, the \( R_{p} \) will not be asymptotic.

The best we can expect to find is an intermediate region in which \( r \) is large enough for \( R_{p} \) to be asymptotic, but not so large that \( R_{p} \) is inaccurate. Accordingly, in Fig. 5 we have plotted \( R_{p}/R_{p} \) vs \( 1/r \), and in Fig. 6, \( R_{p}/R_{p} \) vs \( r \), for various NRO's taken from the "3-9" G limit. The logarithmic derivatives have been plotted versus \( 1/r \), since such plots would be straight lines at \( 1/r = 0 \), with the intercept being the orbital exponent, if \( R_{p} \) goes like a power of \( r \) times an exponential, and if Eqs. (29) were valid.

We see in Fig. 6 an intermediate region that suggests a constant asymptotic ratio. Note especially that there is a large decrease in magnitude in the \( R_{p} \) as \( r \) increases. The logarithmic derivatives in Fig. 5, however, display a much more noticeable sensitivity to the inaccuracies at large \( r \), especially as \( l \) and \( \nu \) increase. The dashed lines are \(-1.344 + (-0.26 - \ln 1 + 5.5)/r\), where \( z = 1.344 \) has been calculated from the exact non-relativistic electronic ionization potential (0,9037 a.u.). In the Hartree-Fock case, the formula for \( \beta \) is \(-1 + 0.26 \), and from this formula we have obtained here \( \beta = 0.26 \). With some imagination, Fig. 5 can be taken as evidence for an \( r^{-2} e^{-4} \) asymptotic behavior for \( R_{p}/R_{p} \), but the evidence is admittedly not definitive.

### VI. NATURAL ORBITAL ENERGY INCREMENTS

In this section we discuss the numerology of the NRO energy increments \( \Delta E_{pi} \) [Eq. (17)]. The numerical values appear in Tables III-V, and comparable, but not identically defined values calculated by Bunge and Ahlrichs, Kutzelnigg, and Bingel are listed in Table VI.

We shall comment first on the accuracy of the \( \Delta E_{pi} \), then on their dependence on "I" limit, third on a remarkably simple empirical formula, fourth on the convergence rate of the CI expansion, and fifth on the non-monotonic behavior of \( \Delta E_{pi} \) as a function of \( l \).

#### A. Accuracy of \( \Delta E_{pi} \)

Errors in the \( \Delta E_{pi} \) of Tables III-V arise primarily from two sources: inadequacy of the original MOUND basis; and inadequacy of the truncated NRO bases.

The errors in the "2-9" \( \Delta E_{pi} \) can be analyzed in detail by comparing them with the "3-9" \( \Delta E_{pi} \), which by Eq. (11) are more accurate. The differences between the "2-9" and "3-9" \( \Delta E_{pi} \) are listed in Table VII. Consider first the S-limit results (the first column of differences), which are direct measures of the inadequacy of the "2-9" basis. Agreement is to within 10\(^{-7}\) a.u., except for the 1s and 2s NRO's, for which the differences are 6.6 \times 10\(^{-7}\) and 2.3 \times 10\(^{-6}\) a.u., respectively. The inadequacy of the "2-9" basis is most severe for the largest \( \Delta E_{pi} \), and less severe for the smaller \( \Delta E_{pi} \). The error in \( \Delta E_{10} \) is consistent with the HF error of 6.6 \times 10\(^{-7}\) a.u., for the same basis.

Next the effect on the s-\( \Delta E_{pi} \) of truncating the s basis to 9 NRO's, the \( p \) basis to 10 NRO's, etc., can be seen by examining the P- through G-limit columns. The discrepancies are now much greater: 1.9 \times 10\(^{-7}\) a.u., for 1s, 1.5 \times 10\(^{-7}\) a.u., for 2s, 2.7 \times 10\(^{-7}\) a.u., for 3s, and less than 10\(^{-7}\) a.u. for all the rest except the last (\( \Delta E_{pi} \)), which shows the severest effect of the truncation. The truncation error is really the result of two processes that go on simultaneously: the CI wave function in the "2-9" calculation has many fewer configurations that in the "3-9" calculation, which in itself would lead to different values of the \( \Delta E_{pi} \); and the (9-dimensional) s basis does not change from the S limit to the G limit and is certainly not adequate for the last s-NRO in the G-limit wave function.

For the \( p \)-NRO's, the first three "2-9" \( \Delta E_{pi} \) have discrepancies of the order of 9 \times 10\(^{-7}\) a.u., 8 \times 10\(^{-7}\) a.u., and 1 \times 10\(^{-6}\) a.u., respectively, while the remaining "2-9" \( \Delta E_{pi} \) are accurate to within 10\(^{-7}\) a.u., except for the last one or two, whose (truncation) errors grow larger as the "I" limit increases.

For higher \( l \) NRO's, the "2-9" \( \Delta E_{pi} \) (whose magnitudes are decreasing) are generally accurate to within 10\(^{-8}\) a.u., except for \( \Delta E_{20,3} \), whose errors are 6 \times 10\(^{-9}\) a.u., and 3 \times 10\(^{-8}\) a.u. The accuracy of the last one or two NRO's with a given \( l \) always deteriorates as the "I" limit increases, because of basis inadequacy.

The above analysis applies to \( l \leq 4 \). Since the errors seem to be decreasing as \( l \) increases, we assume that for \( 5 \leq l \leq 8 \), the errors in the "2-9" \( \Delta E_{pi} \) are less than 10\(^{-8}\) a.u., except perhaps for the last \( \Delta E_{20,3} \). For \( l = 9 \), 10, and 11, the bases were initially taken of dimensions 10, 10, and 9, rather than 27 (see Sec. IV C), and the corresponding \( \Delta E_{pi} \) would not be expected to be as reliable as for \( l \leq 8 \).
TABLE V. Energy increments $\Delta E_L^N$ associated with natural radial orbitals, displayed to illustrate changes from $l=0$ to $l=6$ limit wavefunctions, calculated with "s-p" basis, in atomic units.

<table>
<thead>
<tr>
<th>orbital</th>
<th>L-limit</th>
<th>D-limit</th>
<th>G-limit</th>
<th>H-limit</th>
<th>L-limit</th>
<th>L-limit</th>
<th>L-limit</th>
<th>L-limit</th>
<th>O-limit</th>
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<tbody>
<tr>
<td>2s</td>
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</table>


Total P: $-0.02157486 - 0.02158611 - 0.02158644 - 0.02158639 - 0.02158635 - 0.02158631 - 0.02158569 - 0.02158562 - 0.02158562

Total D: $0.00225496 - 0.00225577 - 0.00225651 - 0.00225695 - 0.00225687 - 0.00225693 - 0.00225721 - 0.00225759

Total F: $0.00005552 - 0.00005556 - 0.00005561 - 0.00005565 - 0.00005569 - 0.00005565 - 0.00005563 - 0.00005563 - 0.00005563

Total G: $0.00000317 - 0.00000317 - 0.00000317 - 0.00000317 - 0.00000317 - 0.00000317 - 0.00000317 - 0.00000317 - 0.00000317

Total H: $0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000

Total K: $0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000 - 0.00000000


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To summarize, the "2-0" $\Delta E_{ul}$ appear to be accurate to 10$^{-5}$ a.u. for $l = 0$, 10$^{-8}$ a.u. for 1 $\leq$ $l$ $\leq$ 8, and possibly a little worse for 9 $\leq$ $l$ $\leq$ 11, except for the large $\Delta E_{ul}$ (2 $\times$ 10$^{-6}$ a.u. for 1s and 2s, 3 $\times$ 10$^{-7}$ a.u. for 3s, 10$^{-8}$ a.u. and 10$^{-7}$ a.u. for the first two p orbitals, 3 $\times$ 10$^{-8}$ a.u. for the first d orbital) and for the last one or two $\Delta E_{ul}$ for each $l$ value.

We cannot assess the accuracy of the "3-0" $\Delta E_{ul}$ as easily, for lack of a more accurate comparison calculation. One can observe that the HF error for the "3-0" basis is 2.4 $\times$ 10$^{-9}$ a.u. (vs 6.8 $\times$ 10$^{-7}$ a.u. for the "2-0" basis), and one could speculate that the error in the "3-0" $\Delta E_{ul}$ is of the order of 10$^{-9}$ a.u. for $l = 0$, 1, 2, and 3 $\times$ 10$^{-8}$ a.u. for $l = 4$, 5.

B. Variation of $\Delta E_{ul}$ as a function of "L"-limit

There is a mild dependence of $\Delta E_{ul}$ on the "L" limit—typically a 1-5% total variation—that can easily be seen in the rows of Tables III-V. The largest changes in a given $\Delta E_{ul}$ occur at the "1+1" and "2+2" limits.

The s-$\Delta E_{ul}$, however, show a greater variation. For example, $\Delta E_{1s,0}$ changes from $-1.24 \times 10^{-7}$ a.u. to $-1.02 \times 10^{-7}$ a.u. in passing from the S to the G limit, a change of 18%.

One should also note that for $\Delta E_{ul}$ that are large in magnitude, even a small percentage change can be large. For example, $\Delta E_{1s,0}$ changes from $-2.86153$ a.u. to $-2.86165$ a.u. in passing from the S to G limit: the percent change is only 0.004%, but the absolute change of 1.2 $\times$ 10$^{-8}$ a.u. is larger than every $\Delta E_{ul}$ for $\nu \geq 5$.

<table>
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<tr>
<th>$\nu$</th>
<th>$\Delta E_{ul}$ (Present)$^b$</th>
<th>$\Delta E_{ul}$ (Bunge)$^b$</th>
<th>$\Delta E_{ul}$ (ABX)$^b$</th>
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$^a$The definitions of the $\Delta E_{ul}$ are not identical. That of Bunge$^b$ is closer to the present one than that of Ahlrichs, Kutselnig, and Bunge.$^b$

$^b$For $\nu$ = 0, 1, and 2, the $\Delta E_{ul}$ (present) are taken from the D-limit column of Table III, while for $\nu$ = 3 and 4, the G-limit column is used.

$^c$Table 7 of Ref. 27.

$^d$Table 3 of Ref. 24.
C. Empirical formula for $\Delta E_{\nu l}$

That $\Delta E_{\nu l}$ should behave systematically for large $\nu$ and $l$ is not surprising and is useful for extrapolations. But it is remarkable that the behavior is given by the simple formula,

$$\Delta E_{\nu l} \sim -a(l + \frac{1}{2})(\nu + l - \frac{1}{2})^6,$$

with

$$a = 0.42, \quad (l \geq 1),$$

$$a = 0.48, \quad (l = 0).$$

The simplicity of Eq. (30) might tempt one to conjecture that there may be a more analytic, less brute force approach to the $\Delta E_{\nu l}$, in which Eq. (30) would be the first term in a series expansion. Formulas similar to Eq. (30) were first discussed by Bunge, who found that for $l = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10$,

$$\Delta E_{\nu l} \sim -A_l(\nu + l + b_l)^6, \quad (\nu \geq 2); \quad \text{Bunge}^{27},$$

where $A_l$ and $b_l$ are constants. We found the fit not to be too sensitive to $b_l$, and we set $b_l = -\frac{1}{2}$.

It is easy to demonstrate the appropriateness of Eq. (30) or (33) by plotting $-\log(-\Delta E_{\nu l})$ vs $\log(\nu + l - \frac{1}{2})$, as in Fig. 7. The curves drawn through the points with constant $l$ show an initial curvature (over a range in $\nu$ that increases with $l$) and then tend to straighten out with a slope of approximately 6. Another demonstration is Table VIII in which $(l + \frac{1}{2})(\nu + l - \frac{1}{2})^6$ $\Delta E_{\nu l}$ is given for various $\nu$, $l$, and "$L$" limits. Equation (30) clearly holds only approximately (it is no good for $\nu = 1$ or 2), but the values in Table VIII are remarkably constant. It is essentially from the $O$-limit column of Table VIII that we have taken the values $a = 0.42$ a.u., $l(>0)$, $0.48$ a.u., $l(=0)$.

We close this subsection with a heuristic discussion of Eq. (30). In Sec. VII we shall see that $\Delta E_{\nu l} \sim -0.074(L + \frac{1}{2})^4$ a.u. Then with Eqs. (29) and (33) we can write

$$\Delta E_{\nu l} \sim -A_l \sum_{m=1}^{l} (\nu + l + b_l)^6,$$

$$\sim A_l \int_{1}^{\nu} (\nu + l + b_l)^6 \, d\nu,$$

$$= -\frac{1}{6} A_l (l + l + b_l)^6,$$

$$\sim -0.074(l + \frac{1}{2})^4, \quad (37)$$

A simple way for Eq. (36) and (37) to be consistent would be for $b_l$ to be $-\frac{1}{2}$, and for $A_l(l + \frac{1}{2})^4$ to be $5 \times 0.074$ a.u., which is not too different from the empirical value of 0.42 a.u. Equations (34)–(37) are of course not meant to be a derivation, but a rough motivation for the empirical formula (30).

Since every NRO, $r^2 R_{nl}$, corresponds to $2l + 1$ NO's one could define an energy increment per NO $\Delta E_{\nu l}$ by

$$\Delta E_{\nu l} = \Delta E_{\nu l}/(2l + 1), \quad (m = l, l - 1, \ldots, -l).$$

Then one could write

$$\Delta E_{\nu l} \sim -\frac{1}{6} a (\nu + l - \frac{1}{2})^6,$$

$$\sim \frac{1}{6} a (\nu - \frac{1}{2})^6.$$

FIG. 7. The $(\nu + l - \frac{1}{2})^6$ behavior of $\Delta E_{\nu l}$: $-\log(-\Delta E_{\nu l})$ vs $\log(\nu + l - \frac{1}{2})$, with $\Delta E_{\nu l}$ from the "$3^{-}3^{-}$" $O$ limit or the "$2^{-}2^{-}$" $O$ limit, depending whether $l = 0, 1, 2, 3, 4$, or $l = 8$. The cases $l = 5, 6, 7$ have been omitted for clarity. They would have fallen between the $l = 4$ and $l = 6$ curves. Also, the $\Delta E_{\nu l}$ for 1s, 2s, and 1p have been omitted to keep the scale reasonable for the other $\Delta E_{\nu l}$.


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The table represents the electric transition probabilities in 16O from the 2S-2P O-limit series, in atomic units.
TABLE VIII (Continued)

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<th>orbital 5-limit</th>
<th>F-limit</th>
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</table>

That is, the energy contribution of each natural orbital is proportional to the inverse sixth power of its principal quantum number.

D. Convergence and extrapolation of the CI expansion for $\Delta E_L$

The empirical formula (30) for $\Delta E_{pL}$ provides a simple way both to extrapolate the calculated $\Delta E_{pL}$ and to estimate the number of terms required in the CI expansion to achieve a prespecified accuracy. From Eqs. (17)–(20) we can write,

$$\Delta E_L = \sum_{\nu=0}^{\infty} \sum_{l=0}^{\nu+1} \left[ \Delta E_{\nu} \left( \text{"L" limit} \right) - \Delta E_{\nu} \left( \text{"L-1" limit} \right) \right]$$

$$+ \sum_{\nu=0}^{\nu_{\text{max}}} \Delta E_{\nu} \left( \text{"L" limit} \right) + \sum_{\nu=\nu_{\text{max}}+1}^{\infty} \Delta E_{\nu} \left( \text{"L" limit} \right).$$

(41)

For extrapolation, we use Eq. (30) for the last term:

$$\sum_{\nu=\nu_{\text{max}}+1}^{\infty} \Delta E_{\nu} \left( \text{"L" limit} \right) \approx -\alpha(L+\frac{1}{2}) \sum_{\nu=\nu_{\text{max}}+1}^{\infty} (\nu + L - \frac{1}{2})^{-5} \tag{42}$$

$$- \frac{1}{5} \alpha(L+\frac{1}{2})(v_{\text{max}}+L)^{-5}. \tag{43}$$

Either Eq. (42) or (43) gives explicitly the amount of the extrapolation, and implicitly, the number of $L$-NRO's required for a given accuracy $\epsilon$, viz.,

$$v_{\text{max}} = \left( \frac{\alpha(L+\frac{1}{2})}{5 \epsilon} \right)^{1/5} - L. \tag{44}$$

Equation (44), moreover, illustrates quantitatively a conjecture by Schwartz, that the convergence is slower (more terms are needed for the same accuracy) as $L$ increases, although eventually the $\Delta E_L$ will be so small that $v_{\text{max}}$ will stop increasing and decrease to zero.

E. Nonmonotonicity of $\Delta E_{\nu}$ as a function of $L$

Bunge\textsuperscript{7} postulated a "golden rule" that included the inequality

$$-\Delta E_{\nu} > -\Delta E_{\nu+1}, \quad \text{(Bunge).} \tag{45}$$

But the inequality already fails for $\nu = 7$ and $l = 0$ at the $P$-limit stage (Table III),

$$-\Delta E_{\nu} = 3.3 \times 10^{-8} \text{ a.u.} < 3.6 \times 10^{-8} \text{ a.u.} = -\Delta E_{\nu+1}. \tag{46}$$

Bunge did not have a large enough number of NRO's to see the $P-\Delta E_{pL}$ overtake the $s-\Delta E_{sL}$, however, it is easy to see from Eq. (30) that $-\Delta E_{\nu} > -\Delta E_{\nu+1}$ for small $\nu$, but that the reverse is true for large $\nu$.

VII. "L"-LIMIT ENERGIES; CONVERGENCE RATE OF THE CI EXPANSION

The CI energies obtained with all configurations with $l \leq L$, the so-called "L"-limit energies $E_{kL}$, are listed in Table IX. As far as we have been able to determine, these "L" limits are more accurate than any previously published, the best of which\textsuperscript{38,32} we have also listed in Table IX. We shall deal in turn with the accuracy of these $E_{kL}$, the $L$ dependence of the $\Delta E_L$, and the convergence rate of the CI expansion.

A. Accuracy of the $E_L$: extrapolated values for $\Delta E_L$ and $E_L$

Before discussing the $L$ dependence of the $\Delta E_L$, we first estimate corrections along the lines developed in Sec. VI D. From the discussion of errors in the $\Delta E_{pL}$ given in Sec. VI A, we expect the errors in the accurately calculated $\Delta E_{pL}$ to be much smaller than the sum of the omitted $\Delta E_{\nu} \left( \nu = v_{\text{max}} + 1 \right)$ to $\infty$. (Note that for $L = 0, 1, 2, 3$, and 4, the $\Delta E_L$ are calculated from "3-9" wave functions, whereas for $L \geq 5$, the $\Delta E_L$ are calculated from "2-9" wave functions.) Consequently we ignore basis inadequacy and use Eqs. (41) and (42) to extrapolate $\Delta E_L$:
**TABLE II.** \(1^L\)-limit energies \(E_L\), increments \(\Delta E_L\), and errors, in atomic units.

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<th>(E_L^{(\text{extrapolated})})</th>
<th>(E_L^{(\text{simple formula})})</th>
<th>(\Delta E_L^{(\text{simple formula})})</th>
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\(^a^\text{See Sec. IV of the text for a description of the basis set.}\) \(\text{The S- through G-basis limit with } J=3\) \(J=9\) bases; the \(\text{H- through Q-basis limit with } J=2\) \(J=6\) bases.

\(^b^\text{Reference 32.}\)

\(^c^\text{Reference 12.}\)

\(^d^\text{Reference 13.}\)

\(\Delta E_L^{(\text{extrapolated})} = \sum L \Delta E_L^{(\text{extrapolated})}.\) See Note j below.

\(^e^\text{This column gives an estimate of the error in the } \Delta E_L^{(\text{bare})} \text{ limit obtained here by CI.}\)

\(^f^\text{The "simple formula" for } \Delta E_L \text{ in Eq.} (51) \text{ of the text, with the constants } a \text{ and } b \
\text{given by 0.07400293 a.u. and 0.02167075 a.u., respectively. (See Ref. 30.) Note that these constants were determined by least squares fitting to the data.}\)

\(\Delta E_L^{(\text{unbalanced})} = \text{Eq.}(31) \text{ formula}, \text{the simple formula for } E_0 \text{ is } E_L^{(\text{extrapolated})} + \sum L \Delta E_L^{(\text{simple formula})}.\)

\(^g^\text{Reference 1.}\)

\(^h^\text{Reference 1.}\)

\(\Delta E_L^{(\text{unbalanced})} = \text{Eq.}(31) \text{ formula}, \text{the simple formula for } E_0 \text{ is } E_L^{(\text{extrapolated})} + \sum L \Delta E_L^{(\text{simple formula})}.\)

\(\Delta E_L^{(\text{extrapolated})} = \sum L \Delta E_L^{(\text{extrapolated})}.\)

Finally from the calculated and extrapolated \(E_L\), one gets the error estimate.

**Estimated error in CI } E_L^{(\text{extrapolated})} - E_L^{(\text{"L" limit CI})} \text{ as follows.}\)

The extrapolated values and error estimates are all included in Table IX, along with two sets of nonextrapolated \(\Delta E_L\) for comparison.

**B. \(L\) dependence of \(\Delta E_L\)**

On the basis of second order perturbation theory\(^7\), Schwartz derived the formula

\[ E_L^{(\text{II})} = -\frac{45}{256} (L + \frac{1}{2})^4 \left[ 1 - \frac{19}{8} (L + \frac{1}{2})^4 + O(L^6) \right]. \]

We find a similar relation for the nonperturbative \(\Delta E_L\).

\[ \Delta E_L = -0.074(L + \frac{1}{2})^4 - 0.031(L + \frac{1}{2})^6. \]

The two constants\(^8\) were obtained by least squares fit to \(\Delta E_L^{(\text{extrapolated})}\) for \(5 \leq L \leq 8\). We chose the upper limit to be 8, because the \(L = 9, 10, 11\) calculations were less accurate. It would be desirable not to have too small a lower limit, since the \(\Delta E_L\) would not be sufficiently asymptotic, but we wanted at least four terms.
to fit. The compromise was to take the lower limit to be 5. The $\Delta E_L$ given by Eq. (53)²⁴ are in excellent agreement with $\Delta E_L$ (extrapolated) for $L = 4$ to 11, and in fair agreement for $L = 1, 2,$ and 3. Thus the $(L + \frac{1}{2})^4$ asymptotic behavior appears to be established, although the reader should note that the coefficient of $(L + \frac{1}{2})^4$ is approximately half of Schwartz's second-order value, and that the second term is $(L + \frac{1}{2})^2$, rather than $(L + \frac{1}{2})^3$. The inverse fifth term gives a better fit than an inverse sixth term. There is not sufficient accuracy to obtain a three-term (inverse fourth, fifth, and sixth) fit, which would be more definitive.

As a further consistency check, we have calculated $E_L$ (extrapolated) as a function of $L$,

$$E_L (\text{extrapolated}) = E_L (\text{extrapolated}) - \sum_{L = 1}^{\infty} \left[ 0.074(L + \frac{1}{2})^4 + 0.031(L + \frac{1}{2})^3 \right].$$  

(54)

The values reported in Table IX are within $1.4 \times 10^{-7}$ a.u. of the exact value for $L = 3$ to 11.

C. Convergence rate of the CI expansion

Let us now try to illustrate the rate of convergence of the CI expansion. The two key equations are Eq. (30) for $\Delta E_L$, an inverse sixth power law, and Eq. (53) for $\Delta E_L$, an inverse fourth power law. From Eq. (30), we derived an estimate of the number of NRO's for quantum number $L$ required to give $\Delta E_L$ to accuracy $\epsilon$, Eq. (44), a $\epsilon^{-1/3}$ law for $N_{\text{max}}$. Similarly one can derive from Eq. (54) an estimate of the $L_{\text{max}}$ for which $E_{\text{max}} - E$ is first less than a given number $\epsilon$, which turns out to be an $\epsilon^{-1/5}$ law for $L_{\text{max}}$.

$$E_{\text{max}} - E \sim \sum_{L_{\text{max}} = 1}^{\infty} 0.074(L + \frac{1}{2})^4,$$

(55)

$$\sim 0.02467(L_{\text{max}} + 1)^2,$$

(56)

$$\sim \epsilon,$$

(57)

$$L_{\text{max}} \sim (0.02467/\epsilon)^{1/5} - 1.$$  

(58)

With the two relations [(58) and (44)] we can estimate how many configurations are needed for a CI energy to have a prescribed accuracy. It is necessary, however, to make a judgement how to apportion the error among the various $\Delta E_L$. For the purpose of illustration we choose $L_{\text{max}}$ so that $\Delta E_{L_{\text{max}}} = \frac{1}{2}$ the total error, and we apportion the remaining $\epsilon$ equally among the $L_{\text{max}} + 1$ $\Delta E_L$ with $L = 0$ to $L_{\text{max}}$:

$$L_{\text{max}} \sim 0.02467(0.75\epsilon_{\text{total}})^{1/5} - 1,$$

(59)

$$\nu_{\text{max}} (L) \sim \left[ -0.42(L + \frac{1}{2})(L + 1) \right]^{1/5} - L,$$

(60)

Total number of NRO's for error $\epsilon_{\text{total}}$

$$\sim \sum_{L_{\text{max}}}^{L_{\text{max}} + 1} \nu_{\text{max}} (L),$$

(61)

Total number of ordinary configurations

$$\sim \sum_{L_{\text{max}}}^{L_{\text{max}} + 1} \frac{1}{2}(\nu_{\text{max}} + 1)\nu_{\text{max}}.$$  

(62)

Estimates based on Eqs. (59)–(62) appear in Table X. The estimates for an accuracy of $2 \times 10^{-3}$ are not too different from the present "2-9" O-limit calculation, despite the crudeness of the Eqs. (59)–(62). The slowness of the convergence is clearly apparent in that a decrease in the error by a factor of ten requires an increase in the number of configurations by a factor of ten. A CI calculation of the accuracy of the Frankowski–Pekeris table energy ($-1.012$ a.u.) is clearly out of reach by even the most optimistic extrapolation of electronic computing technology.

A point not to be overlooked is the regularity of the CI convergence that makes extrapolation straightforward. The two-orders-of-magnitude gain in accuracy by extrapolating the energy (Table IX) somewhat mitigates the slowness of the convergence. A second point is that CI is generally applicable whereas the $\tau_\text{CI}$, logarithm-dependent wave functions are difficult to extend beyond helium.

D. Total energy

Total energies for the ground state of helium, calculated by both CI and non-CI methods, are listed in Table XI. The list²³,²⁴,²⁵,²⁶,²⁷,²⁸,²⁹,³⁰–³⁶ is representative, not exhaustive.

The first CI calculation appears to be that of Hyllebo³⁵ in 1928 (–2.8902 a.u.). Now lower CI energy seems to appear in the literature until the rather non-standard calculation of Tycko, Thomas, and King³⁶ in 1958, whose value of –2.90344 a.u. has apparently not been surpassed by CI until this work (–2.90370 a.u.). Most of the many CI calculations on helium have not been aimed at obtaining an excellent energy, but rather at finding an efficient basis or at making some other point, because non-CI methods have proven much more efficient. Some representative²³,²⁴,²⁵,³¹–³⁶ non-CI calculations have also been summarized in Table XI.

VIII. EMPIRICAL FORMULA FOR THE CI COEFFICIENTS $c_n$

Bunge suggested that the expansion coefficients $c_n$ of Eq. (12) satisfy the formula

$$c_n \sim A_n (b_n + \nu + 1)^{-n},$$

(63)

$n_0 = 4,$  

$n_1 = 5,$  

($n \geq 1$).
TABLE II. Comparison of configuration interaction and non-configuration interaction energies for the helium ground state.

<table>
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<tr>
<th>Energy</th>
<th>Reference No.</th>
<th>Author (year)</th>
<th>Basis</th>
<th>Number of configurations or terms</th>
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<td>-2.897</td>
<td>5</td>
<td>Taylor and Parr (1952)</td>
<td>STO: 1s^22p^34f</td>
<td>4</td>
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<td>-2.1012</td>
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<td>Shull and Lowdin (1959)</td>
<td>Single exponential Laguerre: s^4 p^4 f</td>
<td>20 10</td>
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<td>-2.10170</td>
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<td>Davidson (1963)</td>
<td>NRO s^4 p^4 ; from single exponential Laguerre: s^4 p^4 13</td>
<td>6</td>
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<td>-2.0261</td>
<td>36</td>
<td>Cressy, Miller, and Ruedenberg (1969)</td>
<td>STO: 1s-4p2s-4p3d-4d4f</td>
<td>20 10</td>
</tr>
<tr>
<td>-2.0276</td>
<td>27</td>
<td>Hunge (1970)</td>
<td>NRO s^4 p^4 6 ; from STO: 1s^2 2s^2 2p^2 2d^2 4s-4s 4p^2 2p^2 4p^2 3d^2 4s^2 4d</td>
<td>85 21</td>
</tr>
<tr>
<td>-2.0276</td>
<td>71</td>
<td>Wohlet and Watson (1958)</td>
<td>STO: 1s^2 2s^2 2p^2 3p^2 4f^2 6f</td>
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<td>Weiss (1961)</td>
<td>STO (common exponential within groups): (1e2p1s2p1p1) (1e2p1p1s1) (1p1s1)</td>
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<td>Ahlrichs, Kutzelnigg, and Singel (1966)</td>
<td>NRO s^4 p^4 6 p^2 8 s^2 14 f^2 1 from STO; (not given)</td>
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<td>Green, Kolchin, and Johnson (1965)</td>
<td>STO: 6s^2, 6p^2, with various orbital exponents</td>
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<tr>
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<td>Tyson, Thomas, and King (1958)</td>
<td>Single exponential Laguerre: s^2 10 16 ... 0</td>
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<td>-2.0370</td>
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<td>This work, Carroll, Silverstone, and Metzger (1979)</td>
<td>NRO s^4 p^4 10 10 16 10 12 12 16 18, from 2-9 piezepolynomial; s^4 p^4 10 16 ... 0</td>
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Non-configuration interaction

- 2.90324 | A1 | Hylleraas (1929) | "Hylleraas" | 6 |
- 2.90326 | 33 | Morrell, Norris, and Parr (1976) | Hyperspherical coordinates | 65 |
- 2.903725 | 42 | Kinoshita (1957) | "Kinoshita" | 39 |
- 2.903725 | 22 | Davidson (1963) | "Kinoshita" | 44 |
- 2.9037242 | 43 | Sims, Magstrom, and Hubble (1976) | CI-"Hylleraas" | 88 |
- 2.90372435 | 44 | Scherr and Knight (1963) | Perturbation theory to 13th order | 88 |
- 2.90372475 | 45 | Pekeris (1959) | "Hylleraas-Pekeris" | 1078 |
- 2.9037247616 | 46 | Schwartz (1962) | "Hylleraas-Pekeris" with (r^1 e^1) 1/2 terms | 189 |
- 2.903724770326 | 3 | Frankowski and Pekeris (1965) | "Hylleraas-Pekeris" with logarithmic terms | 246 |

We find, in the same spirit as for Eqs. (30)-(32) for \( \Delta E_{CI} \), a simpler, more general result,

\[
c_{n+l} \sim g(l + \frac{1}{2})^{2/3} (\mu + l - \frac{1}{2})^{4}, \tag{64}
\]

\[
g = 0.35, \quad (l \geq 1), \tag{65}
\]

\[
g = 0.43, \quad (l = 0). \tag{66}
\]

In support of Eqs. (64)-(66), we present in Table XII the quantities \((l + \frac{1}{2})^{2/3} (\mu + l - \frac{1}{2}) c_{n+l}\) for the "2-9" O-limit series.

In Fig. 8 we have plotted \(-\log(-c_{n+l})\) vs \(\log(\mu + l - \frac{1}{2})\). Note that the curves for the \(c_{n+l}\) straighten out visibly sooner than the curves for \(\Delta E_{CI}\) in Fig. 7.

IX. DISCUSSION

Information tabulated in this paper pertains to NRO's with 177 distinct pairs of indices \((\nu, l)\). Such an extensive set of calculations was made possible by the use of piecewise polynomial basis functions, whose principal advantages are flexibility and numerical stability.

The "choice of basis" within the PP framework is the
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TABLE XII (Continued)

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</tbody>
</table>

choice of mesh and degree. The degree should be as high as one can afford (at least for degrees up to 7), and we have used degrees of 2s + 1 = 5 and 7 here. The "rule of thumb" appropriate for the mesh here was to have as few nodes of the NRO's as possible in each subinterval. When a given \( R_n \) had more than \( s \) nodes in any subinterval, the NRO tended to be more inaccurate.

Spatial properties of the NRO's have both intrinsic interest and relevance to the choice of efficient basis functions. Some properties such as localization and the weakness of the dependence of \( r^{-1} R_{nl} \) on \( l \) were already known previously and receive here mainly graphic emphasis (Figs. 3 and 4). Other properties, such as the bunching phenomenon of the nodes (Fig. 2) seem not to have been noticed previously. The tails of the NRO's have already received some theoretical debate to which we contribute a new twist (Eqs. (29a) and (29b), and the discussion following) and some numerical support (Figs. 5 and 6).

The pronounced localization of the NRO's and their peaking towards the origin (Fig. 4) do clearly point out a drawback of "single-exponential" bases. Such bases are equivalent to the basis of nodeless radial functions \([ e^{-r}, r e^{-r}, r^2 e^{-r}, \ldots, r^s e^{-r} ]\), whose maxima occur at progressively larger values of \( r [0, 1/L, 2/L, \ldots, n/L] \), while the NRO's suggest that nodeless functions whose maxima move to smaller values of \( r \) would be more appropriate.

The energy increments \( \Delta E_{nl} \) associated with each NRO have previously been discussed systematically by Bunge. Our more extensive tabulation (Tables III-VIII) characterizes more definitively their numerical values, dependence on "L" limit, and dependence on \( \nu \) and \( l \). The simple formula for \( \Delta E_{nl} \) (Eqs. (30)-(32), (48), and (49)) goes beyond those of Bunge in extracting the \( l \) dependence from his proportionality constants. The formula is also used for estimating errors and extrapolating "L"-limit energies \( E_L \) (Eq. (47) and Table IX), and it hints at a possible underlying analytical framework.

The "L"-limit energies \( E_L \) obtained here (Table IX) are more accurate than any we could find previously, and the increments \( \Delta E_{nl} \) can be fit by a \(-A(L + 1/2)^4 - B(L + 1/2)^4\) formula (Eq. (53), Table IX) similar to that that suggested by Schwartz on the basis of perturbation theory (although the empirical constants are in significant disagreement with the perturbation theory values). Not only is such a formula useful for extrapolation (Table IX), adding two significant figures to the total CI energy, but also for estimating the maximum \( L \) and (along with the formula for \( \Delta E_{nl} \)) the total number of NRO's and configurations required for a CI energy of a given accuracy (Eq. (58) and (62), and Table X).

The CI expansion coefficients \( c_{nl} \), as do the \( \Delta E_{nl} \), turn out to have an empirical dependence on \( \nu \) and \( l \) that is both simple and intriguing (Eqs. (64)-(66) and Table XII).

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APPENDIX A. INTEGRALS

We give here formulas for overlap, nuclear attraction, kinetic energy, and \( 1/r_{ij} \) integrals with respect to the
APPENDIX B. COMPUTATIONAL DETAILS

Computations were carried out in double precision (62-bit mantissa corresponding to approximately 18 decimal digits) on two DECsystem-10 computers, one with a KL processor (JHU), and one with dual KL processors (UM).

Each CI calculation consisted of seven major parts: (1) evaluation of integrals over primitive functions (see Appendix A); (2) orthogonalization of initial orbitals; (3) transformation to the orthogonal orbitals; (4) construction of the Hamiltonian matrix; (5) solution of the eigenvalue problem for the lowest eigenvalue and eigenvector of the Hamiltonian matrix; (6) determination of the NRO's; and (7) truncation of the NRO basis and retransformation to the truncated NRO basis.

By far, the most costly steps were the two-electron integral transformations, involving, for instance, in the O-limit case a few hours on the KL machine. Transformations were accomplished by adaptations of a method described by Bender involving successive quarter transformations.

The energy eigenvalue and eigenvector were obtained using a slight modification of Shavitt's program EIGEN. The NRO's were obtained by diagonalizing the CI coefficient matrix using the EISPACK program R8.

For the two-electron primitive integrals, we take note of the \( 1 \) coupling and sum over the m quantum numbers:

\[
J_{ij}^{m} = \sum_{m} \left| \phi_{ij}^{m} \right|^{2} + \sum_{\tilde{m}} \left| \phi_{ij}^{\tilde{m}} \right|^{2} = \sum_{m} \left| \phi_{ij}^{m} \right|^{2} + \sum_{\tilde{m}} \left| \phi_{ij}^{\tilde{m}} \right|^{2},
\]

(A10)

We use the Laplace expansion for \( 1/\sqrt{\alpha} \). First assume \( \alpha < \beta \). Then,

\[
J_{ij}^{m} = \sum_{l=0}^{+\infty} \sum_{\lambda=0}^{\infty} \frac{\sqrt{\pi}}{2\lambda+1} \left( \phi_{ij}^{m} \right)^{2} \left( Y_{\lambda}^{M} \right) \left( \phi_{ij}^{\lambda} \right)^{2},
\]

(A11)

where the 3-j symbol is given by

\[
\begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix} = \frac{(-1)^{3-l}}{(2L-2l)(2L-2l')},
\]

(A12)

\[
L = (l + l' + \lambda)/2.
\]

Finally, when \( \alpha = \beta \), we obtain

\[
J_{ij}^{m} = \sum_{l=0}^{+\infty} \sum_{\lambda=0}^{\infty} \frac{\sqrt{\pi}}{2\lambda+1} \left( \phi_{ij}^{m} \right)^{2} \left( Y_{\lambda}^{M} \right) \left( \phi_{ij}^{\lambda} \right)^{2}.
\]

(A13)

\[
L = (l + l' + \lambda)/2.
\]

(A14)

Three alternative, similar formulas can be obtained by carrying out the integrations in Eq. (A15) in different orders.

\[
J_{ij}^{m} = \sum_{l=0}^{+\infty} \sum_{\lambda=0}^{\infty} \frac{\sqrt{\pi}}{2\lambda+1} \left( \phi_{ij}^{m} \right)^{2} \left( Y_{\lambda}^{M} \right) \left( \phi_{ij}^{\lambda} \right)^{2}.
\]

(A15)
APPENDIX C. ADDENDUM ON EQUATIONS (26)–(29)

A derivation of Eqs. (26)–(29) was recently given. In an earlier treatment, Ahlrichs and Driessler in essence obtained the pseudo eigenvalue Eqs. (26)–(28), but context and emphasis veil the similarity. Recently Ahlrichs further developed the approach into a self-consistent direct method.

34The constants actually used to calculate the $\Delta E_x$ in Table IX were 0.07400947 a.u. and 0.03136703 a.u., but we regard 0.0740 and 0.031 to be more indicative of the precision to which $A$ and $B$ have been obtained.
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